IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Masahide KAWARAYA et al.

Appln. No. 10/530,475
Group Art Unit: 2813
Examiner: RODGERS, COLLEEN E
Filed: 04/06/2005

For: PROCESS FOR FORMING SEMICONDUCTOR FILM AND USE OF SEMICONDUCTOR FILM

Commissioner of Patents
PO Box 1450
Alexandria, VA 22313-1450
Sir:

DECLARATION UNDER 37 C.F.R.Section 1.132

I, Iwao HAYASHI, do hereby declare that:

1. I am a Japanese citizen, residing at 4-9-102, Nishihashimoto 3-chome, Sagamihara-shi, Kanagawa, Japan.
2. I graduated from Department of Mechanical Engineering, Faculty of Engineering, Chiba University, Chiba, Japan, in March 1998.
3. I began my employment with KANSAI PAINT CO., LTD., the assignee of the above-identified application in April 1998. Since April 1998, I have been engaged in the research and development of chemistry.
4. I am one of the named inventors of the above-identified application, and am familiar with the subject matter of said application as well as the disclosures in the cited references.
5. The experiments given below were carried out under my general direction and supervision.

Experiments

Experiment 1

(i) A polyethylene terephthalate (PET) film (100 cm long, 30 cm wide and 1 mm thick) was spray-coated with the titanium oxide particle dispersion liquid obtained in the Production Example 1 of the instant specification using a spray coater in which the dispersion liquid was pumped through a spray nozzle (tradename "Aerocoat system", manufactured by Nordson Corporation), under the coating conditions described in the following Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater was 0.8 µm.

The resulting coating was dried in an electric furnace at 150°C for 30 minutes, to thereby obtain a 7 µm thick porous titanium oxide film.

(ii) A 7 µm thick porous titanium oxide film was obtained in the same manner as in (i) except using an electrically conductive PET film on which a 1 µm thick ITO electrically conductive transparent layer had been vapor-deposited as a substrate.

The substrate with the porous film was immersed in an ethanol solution containing a sensitizing dye [Ru(2,2'-bipyridil-4,4'-dicarboxylate(TBA)$)_2$(NCS)] at a concentration of $5x10^{-4}$M/L at room temperature overnight to obtain a photoelectrode. The above-mentioned electrically conductive PET film sputtered with platinum was superimposed as a counter electrode on the sensitizing dye-adsorbing porous titanium oxide film of the photoelectrode.

An electrolyte solution (40 mM iodine, 500 mM tetrapropylammonium iodine, 80 M ethylene carbonate and 20 M acetonitrile) was poured between the titanium oxide film of the photoelectrode and the counter electrode, to obtain a dye-sensitized solar cell.

Experiment 2

(i) Spray coating was performed in the same manner as in Experiment 1 (i) except for using a spray coater in which the dispersion liquid was pumped through a two-fluid spray nozzle (tradename "Atomax Nozzle (Model AM25S)", manufactured by Atomax Co., Ltd.) and employing the coating conditions shown in the following Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater was 28.9 μm.

The resulting coating was dried in an electric furnace at 150°C for 30 minutes, to thereby obtain a 9 μm thick porous titanium oxide film.

The mean pore size of the porous titanium oxide film was measured in the same manner as in Example 1 (i) of the instant specification and found to be 10.3 nm.

(ii) A dye-sensitized solar cell was obtained in the same manner as in Experiment 1 (ii) except for employing the coating conditions shown in Table 1 and forming a 9 μm thick porous titanium oxide film.

Experiment 3

(i) Spray coating was performed in the same manner as in Experiment 1 (i) except for using a spray coater in which the dispersion liquid was pumped through a two-fluid spray nozzle (tradename "Atomax Nozzle (Model AM25S)", manufactured by Atomax Co., Ltd.) and employing the coating conditions shown in the following Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater was 19.5 μm.

The resulting coating was dried in an electric furnace at 100°C for 30 minutes, to thereby obtain a 7 μm thick porous titanium oxide film.

The mean pore size of the porous titanium

oxide film was measured in the same manner as in Example 1 (i) of the instant specification and found to be 9.9 nm.

(ii) A dye-sensitized solar cell was obtained in the same manner as in Experiment 1 (ii) except for employing the coating conditions shown in Table 1 and forming a 7 μm thick porous titanium oxide film.

<u>Experiment 4</u>

(i) Spray coating was performed in the same manner as in Experiment 1 (i) except for using a spray coater in which the dispersion liquid was pumped through a two-fluid spray nozzle (tradename "Atomax Nozzle (Model AM25S)", manufactured by Atomax Co., Ltd.) and employing the coating conditions shown in the following Table 1. The mean diameter of the atomized droplets of the dispersion liquid discharged from the spray coater was 19.5 μm.

The resulting coating was dried in an electric furnace at 200°C for 30 minutes. As a result, the PET film melted and the evaluation could not be conducted.

Table 1

	Experiment			
	1	2	3	4
Discharged amount (g/min)	1	60	60	60
Atomization air pressure (kgf/cm^2)	0.05	1.5	2.0	2.0
Number of stages	3	3	3	3
Nozzle-substrate distance (mm)	55	20	20	20
Coating rate (m/min)	1.2	60	60	60

The porous titanium oxide films obtained in Experiment 1 (i), Experiment 2 (i) and Experiment 3 (i) were tested for adhesion and scratch resistance. The test method was the same method described in the instant specification.

The test results are shown in Table 2.

Table 2

	Experiment			
	1	2	3	4
Mean diameter of the atomized droplets (μm)	0.8	28.9	19.5	19.5
Drying condition	150°C 30 min.		100°C 30 min.	200°C 30 min.
Thick of porous titanium oxide film (μm)	7	9	7	-
Mean pore size (nm)	-	10.3	9.9	-
Adhesion	Poor	Poor	Poor	-
Scratch resistance	2.9	8.2	8.4	-

<u>Consideration of Results</u>

From the results of Experiment 1 (mean diameter of atomized droplets: 0.8 μm) and Experiment 2 (mean diameter of atomized droplets: 28.9 μm), it is apparent that if the mean diameter of the atomized droplets is out of the range of 1 to 25 μm, a semiconductor film with good adhesion to the substrate and high photoelectric conversion efficiency cannot be obtained.

From the result of Experiment 3 (heating temperature: 100 °C), it is apparent that if the heating temperature is lower than 130 °C, a semiconductor film with good adhesion to the substrate and high photoelectric conversion efficiency cannot be obtained. Also, from the result of Experiment 4 (heating temperature: 200 °C), if the heating temperature is higher than 180 °C, thermoplastic resin substrates such as PET film are deformed and degraded.

On the other hand, the Examples of the instant specification show that the semiconductor films of the present invention have good adhesion to the substrate and high photoelectric conversion efficiency.

6. I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: June 18, 2008

By Iwao Hayashi

Iwao HAYASHI